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Allylsucrose: A Potential Upgrader for Drying Oils

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Natural drying oils, particularly linseed oil, have been treated in a number of ways to improve their utility as protective coatings. For many years blowing, heat-bodying and alkali-refining were accepted methods for improving drying properties. Later, copolymerization with unsaturated hydrocarbons, conjugation by catalytic treatment, improved polymerization catalysts, and addition of improved drying oils such as tung oil were introduced. More recently, diallylresorcinol (1) and "Dryene" (2) have been suggested as upgraders for drying oils. In this paper the upgrading of oils by coblowing with allylsucrose,[†] a new synthetic material resembling drying oil, is discussed.

The general concept of functionality in the polymerization field has placed considerable emphasis in drying oil chemistry on the study of polyalcohols other than glycerol. In a recent review article Bolley (3) pointed out that as the functionality of the alcohol increases, the rate of drying and hardness of the films increase, and also that unsaturated fatty esters prepared from erythritol, pentaerythritol, mannitol, sorbitol and inositol are superior to the glycerides. The difficulties encountered in esterifying sugars and starches directly with unsaturated fatty acids have limited investigations mainly to the less complex polyalcohols. In the sugar series Rosenthal and Lenhard (4) tried to avoid this problem by condensing sucrose with linoleoyl chloride in place of the free acid. Rheineck, Rabin, and Long (5) described esterifications of glucose, maltose and sucrose with the acid chlorides of linseed, perilla, China-wood, and rosin acids. However, the products were not characterized in either patent.

In the past four years a new type of synthetic material resembling a drying oil, prepared from sucrose, starch, and other sugar alcohols, which are cheap and abundant raw materials, has been described. Allylsucrose (6) and allyl starch (7) are polyethers with a relatively small unsaturated allyl group in place of the long-chain unsaturated fatty acid in the conventional drying oils. Allyl ethers undergo oxidative polymerization characteristic of drying oils, giving coatings that possess high gloss, extreme hardness

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and good resistance to solvents, oils, and heat (8). These ethers can be prepared in good yield by treating sucrose or starch with allyl chloride in the presence of sodium hydroxide.

Allylsucrose is obtained as a pale yellow oil which can be stored indefinitely without change. When it is deposited on a panel of wood, glass or metal either as such or from a solution in an organic solvent, the film remains tacky for a long time. For coating applications, it is advisable to partially polymerize allylsucrose by blowing with air or oxygen prior to solution in an organic solvent (6b). A suitable method for regulating this operation has been reported (6c). Although partially polymerized allylsucrose gels in a relatively short time, solutions of this blown material in organic solvents can be stored for a long time without deterioration.

The blowing operation, the ready solubility of allylsucrose in organic solvents and its compatibility with drying oils may be utilized for the modification of natural oils. When it was found that allylsucrose is polymerized by oxygen much more rapidly than boiled linseed or dehydrated castor oils, mixtures of allylsucrose and these and other oils were polymerized. The experiments described here suggest that copolymerization takes place between allylsucrose and the unsaturated components of the drying or semi-drying oils.

At room temperature raw or boiled linseed oil, dehydrated castor oil, and soybean oil gave cloudy solutions with allylsucrose in a 1:1 ratio. Allylsucrose propionate (6.5 allyl; 1.0 propionyl) and ethyl allylsucrose (6.5 allyl; 0.7 ethyl) when substituted for allylsucrose gave clear solutions with dehydrated castor oil, and raw and boiled linseed oil, but cloudy solutions with soybean oil. Allylsucrose was completely miscible with oiticica oil in all proportions, but incompatible with tung oil (1:1). When heated, however, tung oil and allylsucrose gave clear solutions. Oiticica oil, composed mainly of glycerides of licanic acid, which possesses a triple unsaturated system plus an isolated polar carbonyl group, showed the greatest compatibility with allylsucrose. When the free hydroxyl groups in allylsucrose were replaced by ester or ether groups (propionyl or ethyl) compatibility with drying oils increased. While most of the drying oils are incompatible with allylsucrose at room temperature, when mixtures of allylsucrose and drying oil were heated, clear solutions were obtained. Blowing these mixtures with oxygen at 100 C. yielded clear products which were soluble in organic solvents. It is thus apparent that compatibility at elevated temperature and the ability of allylsucrose to yield clear products when coblown with other drying oils makes the question of compatibility at room temperature relatively unimportant.

Table I reveals that allylsucrose at 100 C. with oxygen bubbled through it gels a little more slowly than tung or oiticica oil but considerably faster than raw or boiled linseed oil, dehydrated castor oil, and soybean oil. *Table I* shows that the actual gelation times of all the 50-50 mixtures were less than half the sum of the gelation times of the individual components. Oiticica oil, which gels more rapidly than allylsucrose, gels still more rapidly when blown with allylsucrose; tung oil exhibits this tendency to a less degree. A synergistic effect is also noticed in the other mixtures. Equal parts of raw

linseed oil and allylsucrose approximated the gelation time of dehydrated castor oil.

Soybean oil itself gelled in 1275 minutes. When 10, 20, 40, or 50 per cent allylsucrose was added, the gelation time was reduced progressively

*Table I—Gelation Time of Allylsucrose, Various Drying Oils, and Allylsucrose—Oil Mixtures**

	<i>Gelation Time, minutes</i>	<i>Calcd. from Individual Components †</i>
Tung oil	121	
Oiticica oil	136	
Allylsucrose	168	
Allylsucrose propionate	258	
Boiled linseed oil	455	
Dehydrated castor oil	522	
Raw linseed oil	947	
Soybean oil	1275	
50% Tung oil—50% allylsucrose	118	145
50% Oiticica oil—50% allylsucrose	104	152
50% Boiled linseed oil—50% allylsucrose	262	312
50% Dehydrated castor oil—50% allylsucrose	297	345
50% Boiled linseed oil—50% allylsucrose propionate	305	357
50% Soybean oil—50% allylsucrose	381	721
60% Soybean oil—40% allylsucrose	405	832
50% Raw lineed oil—50% allylsucrose	500	558
80% Soybean oil—20% allylsucrose	610	1054
80% Soybean oil—10% allylsucrose—10% tung oil	661	1049
90% Soybean oil—10% tung oil	824	1160
90% Solbean oil—10% oiticica oil	875	1161
90% Soybean oil—10% allylsucrose	903	1164
Soybean oil + 0.2% cobalt‡	367	
50% Soybean oil—50% allylsucrose + 0.2% cobalt‡	131	
Boiled linseed oil + 0.2% cobalt‡	231	
50% Boiled linseed oil—50% allylsucrose + 0.2% cobalt‡	140	

* At 100°C., 7.2 cc.; 7.5 liters of O₂ per hr.

† Assuming a straight line relationship.

‡ Cobalt added as 6% cobalt octoate.

to 903, 610, 405, and 381 minutes. Some of the viscosity changes for the experiments of *Table I* are listed in *Figure 1*. Comparison of curves 5, 7, and 8 illustrates the effect of increased amounts of allylsucrose on the polymerization of allylsucrose—soybean oil mixtures. The effect of small quantities of allylsucrose on the gelation point of soybean oil was then compared with the effects of similar proportions of tung and oiticica oil. In 90-10 mixtures, allylsucrose exerts about the same influence as tung and oiticica oil. It is significant that 50 per cent allylsucrose as an upgrader for

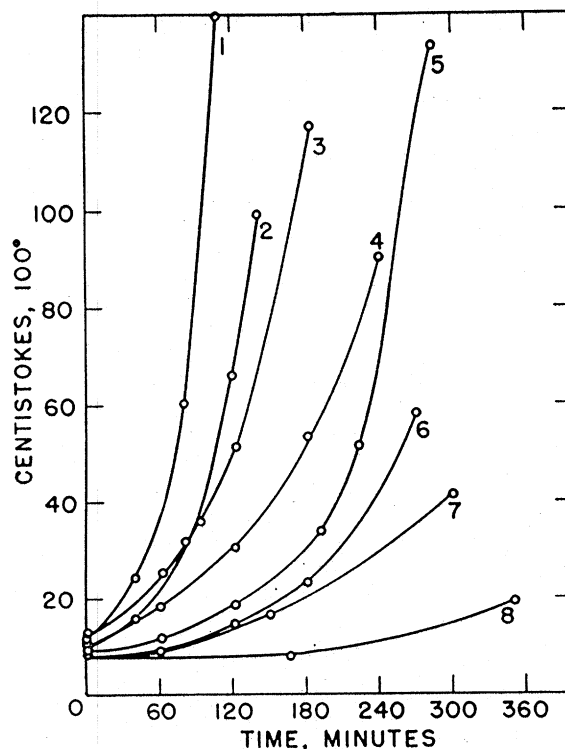


Figure 1.—Change in Viscosity of Allylsucrose-Oil Mixtures During Blowing with Oxygen at 100° C.

1, Allylsucrose; 2, 50% Boiled Linseed Oil, 50% Allylsucrose; 3, 50% Dehydrated Castor Oil, 50% Allylsucrose; 4, Boiled Linseed Oil, 50% Allylsucrose; 5, 60% Soybean Oil, 40% Allylsucrose; 6, 50% Raw Linseed Oil, 50% Allylsucrose; 7, 80% Soybean Oil, 20% Allylsucrose; 8, Soybean Oil.

soybean oil was equivalent to the addition of 0.2 per cent cobalt. Addition of the same amount of cobalt to the 50-50 allylsucrose—soybean oil mixture, however, reduced polymerization time still further. Cobalt gave similar results with linseed oil. Though on superficial examination allylsucrose appeared to have no advantage over cobalt, tung oil, or oiticica oil as far as rate of drying is concerned, preliminary experiments indicated that allylsucrose improves the hardness of films and confers improved resistance to various solvents.

To translate the gelation times to practical terms, properties of films prepared from 50 per cent solutions of various blown mixtures in toluene containing 0.1 per cent cobalt were studied. Blown soybean oil gave films that were tacky after air-drying for two weeks. Although 90:10 and 80:20 soybean oil—allylsucrose mixtures showed no noteworthy improvement, the

drying time at the 50:50 ratio was reduced from two weeks to eight hours. An 80:20 blown mixture of boiled linseed oil—allylsucrose dried in four hours, as compared with twenty-one hours for blown linseed oil itself. The Sward hardness (12-14) of films from allylsucrose mixed with linseed or soybean oil was superior to that from soybean oil (0-1) or linseed oil (2). The resistance of films from the soybean oil—allylsucrose mixtures to water and various organic solvents was superior to resistance of soybean oil or allylsucrose films alone.

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Summary

Allylsucrose, a new synthetic oil, dries more rapidly than most of the common, natural drying oils. Since the addition of allylsucrose to drying oils and subsequent blowing yields products with reduced drying time, improved hardness, and resistance to solvents, allylsucrose is suggested as a potential upgrader for oils such as linseed and soybean oils.

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